

**1047,569**



# PATENT SPECIFICATION

NO DRAWINGS

**1047,569**

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## COMPLETE SPECIFICATION

### Light-Sensitive Compositions

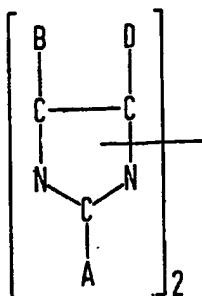
We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is directed to novel light-sensitive compositions and to a unique process for forming a colored material from an essentially colorless one by irradiation with ultraviolet light. More particularly, the present invention is directed to a composition consisting of an intimate admixture of the leuco form of a dye and the dimer of a selected 2,4,5-triarylimidazolyl radical, which composition, in the presence of an inert solvent, quickly undergoes a color change to form a clear image upon irradiation with a pattern of ultraviolet light.

Image-forming compositions and processes play an essential part in photography, thermography and related arts dealing with processes of writing, printing, and producing images with the aid of light, heat, electricity, or combinations of these activating influences. Currently available methods of image production impose numerous limitations which are costly, inconvenient, time consuming, and sometimes potentially hazardous. For example, classical photography, although efficient in the utilization of light energy, employs expensive chemicals and papers, involves multi-step processing and drying, and requires a highly skilled operator for consistently good results.

Thermography requires less operator skill and less expensive papers but produces images of poor quality which are easily destroyed. Mechanical printing, while inexpensive and rapid for repetitive printing, is decidedly more expensive and slow for sequential printing. In both cases, mechanical printing yields a wet image. Presently available photochemical image-forming systems involve the use of toxic chemicals such as ammonia, cyanide derivatives, halogenated hydrocarbons and caustic materials. A new printing image-forming system which would overcome even some of the limitations of the currently available methods would significantly advance the art and be desirable.

According to the present invention we provide a composition which comprises an admixture of (1) a dye in the leuco form having the formula  $DH_n$  where H is a hydrogen atom whose removal forms a compound colored differently to  $DH_n$  and n is 1 or 2 and (2) a 2,4,5-triarylimidazolyl dimer consisting of two imidazolyl units joined together by a single covalent bond, the dimer having the formula:—



wherein the valencies of the atoms in the imidazolyl rings, other than those through which the imidazolyl rings are joined, are satisfied by two conjugated intracyclic double bonds, and where A, B and D, which may be the same or different, are substituted or unsubstituted carbocyclic or heterocyclic aromatic radicals, the dimer being dissociated into free radicals when irradiated with ultraviolet light.

The substituents A, B and D are referred to herein as "aryl" radicals and it is to be understood that this term is used in this specification to include both carbocyclic and heterocyclic aromatic radicals.

A preferred composition of this type is one in which the leuco dye, DH<sub>n</sub>, is an acid addition salt of the leuco form of triphenylimethane dye having in at least two of the phenyl rings and positioned para to the methane carbon atom an amino, alkyl-amino (containing 1 to 4 carbon atoms) or dialkylamino (containing 1 to 4 carbon atoms in each alkyl group) substituent group and the 2,4,5-triarylimidazolyl dimer is the dimer of either:

(a) the 2,4,5-triphenyl imidazolyl radical having an ortho substituent in the 2-phenyl and 2'-phenyl rings, the substituent being a chlorine, bromine or fluorine atom or a methoxy group or an alkyl group containing 1 to 4 carbon atoms, or

(b) the 2-(1-naphthyl)-4,5-diphenylimidazolyl radical.

The leuco dye/biimidazole mixture is dissolved in an inert solvent to make up a solution which is used to impregnate paper; additionally it can be combined with an inert transparent polymeric binder and the resultant composition dissolved in the solvent and used to coat or impregnate substrates.

By irradiating the compositions in the presence of the solvent (either as they are or coated on or impregnated in a substrate) with light having a wavelength of from 2000 Å to 4000 Å, the colors are produced and they can then be fixed to prevent further color formation on irradiation.

The leuco form of the dye which is present in the compositions of the present invention is the reduced form of the dye having one or two hydrogen atoms the removal of which, together with an additional electron in certain cases, produces the dye. Since the leuco form of the dye is essentially colorless, or in some instances it may be of a different color or of a less intense shade than the parent dye, it provides a means of producing an image when the leuco form is oxidized to the dye. This oxidation is accomplished in the invention by having present in intimate admixture with the leuco form of the dye a dimer of a 2,4,5-triarylimidazolyl radical. The dimer of the imidazolyl radical is activated by light in the ultraviolet range of wave length from 2000 Å to 4200 Å, and when irradiated with light within this range it splits into free imidazolyl radicals. These free radicals react with the leuco form of the dye to produce a colored image against a background of unirradiated and, therefore, unchanged material.

A large number of dyes in the leuco form have been found to be readily converted to the parent dye by free 2,4,5-triarylimidazolyl radicals by the above-described mechanism and are well adapted to be used in the image forming compositions. Dyes in the leuco form which are operative according to the invention include

- a. aminotriarylmethanes including
  - (i) carbocyclic aromatic groups and
  - (ii) heterocyclic aromatic groups.
- b. aminoxanthenes
- c. aminothioxanthenes

	d. amino-9,10-dihydroacridines	
	e. aminophenoxazines	
	f. aminophenothiazines	
	g. aminophenothenothiazines	
5	h. aminodiphenylmethanes	5
	i. leucoindamines	
	j. aminohydrocinnamic acids, their esters, amides and cyanoethanes	
	k. hydrazines	
10	l. leuco indigo dyes	10
	m. amino-2,3-dihydroanthraquinones	
	n. tetrahalo-p,p'-biphenols	
	o. 2(p-hydroxyphenyl)-4,5-diphenylimidazole	
	p. phenethylanilines	

Of these leuco forms, a) through i) form the dye by losing one hydrogen atom, while  
 15 the leuco forms j) through p) lose two hydrogen atoms to produce the parent dye.  
 Representative leuco dyes of the above a) through p) groups are:

15	a(i) <i>Aminotriarylmethanes (carbocyclic aromatic groups)</i>	
20	bis(4-amino-2-butylphenyl)(p-dimethylaminophenyl)methane	20
	bis(4-amino-2-chlorophenyl)(p-aminophenyl)methane	
	bis(4-amino-3-chlorophenyl)(o-chlorophenyl)methane	
	bis(4-amino-3-chlorophenyl)phenylmethane	
	bis(4-amino-3,5-diethylphenyl)(o-chlorophenyl)methane	
	bis(4-amino-3,5-diethylphenyl)(o-ethoxyphenyl)methane	
25	bis(4-amino-3,5-diethylphenyl)(p-methoxyphenyl)methane	25
	bis(4-amino-3,5-diethylphenyl)phenylmethane	
	bis(4-amino-3-ethylphenyl)(o-chlorophenyl)methane	
	bis(p-aminophenyl)(4-amino-m-tolyl)methane	
	bis(p-aminophenyl)(o-chlorophenyl)methane	
30	bis(p-aminophenyl)(p-chlorophenyl)methane	30
	bis(p-aminophenyl)(2,4-dichlorophenyl)methane	
	bis(p-aminophenyl)(2,5-dichlorophenyl)methane	
	bis(p-aminophenyl)(2,6-dichlorophenyl)methane	
	bis(p-aminophenyl)phenylmethane	
	bis(4-amino-o-tolyl)(p-chlorophenyl)methane	
35	bis(4-amino-o-tolyl)(2,4-dichlorophenyl)methane	35
	bis(p-anilinophenyl)(4-amino-m-tolyl)methane	
	bis(4-benzylamino-2-cyanophenyl)(p-aminophenyl)methane	
	bis(p-benzylethylaminophenyl)(p-chlorophenyl)methane	
40	bis(p-benzylethylaminophenyl)(p-diethylaminophenyl)methane	40
	bis(p-benzylethylaminophenyl)(p-dimethylaminophenyl)methane	
	bis(4-benzylethylamino-o-tolyl)(p-methoxyphenyl)methane	
	bis(p-benzylethylaminophenyl)-phenylmethane	
	bis(4-benzylethylamino-o-tolyl)(o-chlorophenyl)methane	
45	bis(4-benzylethylamino-o-tolyl)(p-diethylaminophenyl)methane	45
	bis(4-benzylethylamino-o-tolyl)(4-diethylamino-o-tolyl)methane	
	bis(4-benzylethylamino-o-tolyl)(p-dimethylaminophenyl)methane	
	bis[2-chloro-4-(2-diethylaminoethyl)ethylaminophenyl](o-chlorophenyl)methane	
	bis[p-bis(2-cyanoethyl)aminophenyl]phenylmethane	
50	bis[p-(2-cyanoethyl)ethylamino-o-tolyl](p-dimethylaminophenyl)methane	50
	bis[p-(2-cyanoethyl)methylaminophenyl](p-diethylaminophenyl)methane	
	bis(p-dibutylaminophenyl)[p-(2-cyanoethyl)methylaminophenyl]methane	
	bis(p-dibutylaminophenyl)(p-diethylaminophenyl)methane	
	bis(4-diethylamino-2-butoxyphenyl)(p-diethylaminophenyl)methane	
55	bis(4-diethylamino-2-fluorophenyl)o-tolylmethane	55
	bis(p-diethylaminophenyl)(p-aminophenyl)methane	
	bis(p-diethylaminophenyl)(4-anilino-1-naphthyl)methane	
	bis(p-diethylaminophenyl)(m-butoxyphenyl)methane	
	bis(p-diethylaminophenyl)(o-chlorophenyl)methane	
60	bis(p-diethylaminophenyl)(p-cyanophenyl)methane	60
	bis(p-diethylaminophenyl)(2,4-dichlorophenyl)methane	
	bis(p-diethylaminophenyl)(4-diethylamino-1-naphthyl)methane	
	bis(p-diethylaminophenyl)(p-dimethylaminophenyl)methane	

	bis(p-diethylaminophenyl)(4-ethylamino-1-naphthyl)methane	
	bis(p-diethylaminophenyl)2-naphthylmethane	
	bis(p-diethylaminophenyl)(p-nitrophenyl)methane	
5	bis(p-diethylamino-m-tolyl)(p-diethylaminophenyl)methane	5
	bis(4-diethylamino-o-tolyl)(o-chlorophenyl)methane	
	bis(4-diethylamino-o-tolyl)(p-diethylaminophenyl)methane	
	bis(4-diethylamino-o-tolyl)(p-diphenylaminophenyl)methane	
	bis(4-diethylamino-o-tolyl)phenylmethane	
	bis(4-dimethylamino-2-bromophenyl)phenylmethane	
10	bis(p-dimethylaminophenyl)(4-anilino-1-naphthyl)methane	10
	bis(p-dimethylaminophenyl)(p-butylaminophenyl)methane	
	bis(p-dimethylaminophenyl)(p-sec. butylethylaminophenyl)methane	
	bis(p-dimethylaminophenyl)(p-chlorophenyl)methane	
	bis(p-dimethylaminophenyl)(p-diethylaminophenyl)methane	
15	bis(p-dimethylaminophenyl)(4-dimethylamino-1-naphthyl)methane	15
	bis(p-dimethylaminophenyl)(6-dimethylamino-m-tolyl)methane	
	bis(p-dimethylaminophenyl)(4-dimethylamino-o-tolyl)methane	
	bis(p-dimethylaminophenyl)(4-ethylamino-1-naphthyl)methane	
	bis(p-dimethylaminophenyl)(p-hexyloxyphenyl)methane	
20	bis(p-dimethylaminophenyl)(p-methoxyphenyl)methane	20
	bis(p-dimethylaminophenyl) o-tolylmethane	
	bis(4-dimethylamino-o-tolyl)(p-aminophenyl)methane	
	bis(4-dimethylamino-o-tolyl)(o-bromophenyl)methane	
	bis(4-dimethylamino-o-tolyl)(o-cyanophenyl)methane	
25	bis(4-dimethylamino-o-tolyl)(o-fluorophenyl)methane	25
	bis(4-dimethylamino-o-tolyl) 1-naphthylmethane	
	bis(4-dimethylamino-o-tolyl) phenylmethane	
	bis(p-ethylaminophenyl)(o-chlorophenyl)methane	
	bis(4-ethylamino-m-tolyl)(o-methoxyphenyl)methane	
30	bis(4-ethylamino-m-tolyl)(p-methoxyphenyl)methane	30
	bis(4-ethylamino-m-tolyl)(p-dimethylaminophenyl)methane	
	bis(4-ethylamino-m-tolyl)(p-hydroxyphenyl)methane	
	bis[4-ethyl(2-hydroxyethyl)amino-m-tolyl](p-diethylaminophenyl)methane	
	bis[p-(2-hydroxyethyl)aminophenyl](o-chlorophenyl)methane	
35	bis[p-(bis(2-hydroxyethyl)aminophenyl)(4-diethylamino-o-tolyl)methane	35
	bis[p-(2-methoxyethyl)aminophenyl] phenylmethane	
	bis(p-methylaminophenyl)(o-hydroxyphenyl)methane	
	bis(p-propylaminophenyl)(m-bromophenyl)methane	
	tris(4-amino-o-tolyl)methane	
40	tris(4-anilino-o-tolyl)methane	40
	tris(p-benzylaminophenyl)methane	
	tris[4-bis(2-cyanoethyl)amino-o-tolyl]methane	
	tris[p-(2-cyanoethyl)ethylaminophenyl]methane	
	tris(p-dibutylaminophenyl)methane	
45	tris(p-di-t-butylaminophenyl)methane	45
	tris(4-diethylamino-2-chlorophenyl)methane	
	tris(p-diethylaminophenyl)methane	
	tris(4-diethylamino-o-tolyl)methane	
	tris(p-dihexylamino-o-tolyl)methane	
50	tris(4-dimethylamino-o-tolyl)methane	50
	tris(p-hexylaminophenyl)methane	
	tris[p-bis(2-hydroxyethyl)aminophenyl]methane	
	tris(p-methylaminophenyl)methane	
	tris(p-dioctadecylaminophenyl)methane	
55	<i>a(ii) Amino triaryl methanes (heterocyclic aromatic groups).</i>	
	bis(p-diethylaminophenyl)-21pyridylmethane	55
	bis(p-dimethylaminophenyl)(5-methyl-2-pyridyl)methane	
	bis(p-dimethylaminophenyl)2-quinolylmethane	
	bis(p-dimethylaminophenyl)(1,3,3-trimethyl-2-indolinylidenemethyl)methane	

In addition to the aminotriarylmethanes listed above the leuco forms of the triphenylmethane dyes identified by the following Colour Index numbers may be used, 42000B, 42005, 42010, 42025, 42030, 42036, 42035, 42040, 42500, 42505, 42510B, 42515, 42520, 42555B, 42556, 42563B, 42600, 42605, 42705, 42760, 42785, 43500.

5	<b>b. Aminoxanthenes</b>	5
	3-amino-6-dimethylamino-2-methyl-9-(o-chlorophenyl)xanthene	
	3-amino-6-dimethylamino-2-methyl-9-phenylxanthene	
	3-amino-6-dimethylamino-2-methylxanthene	
10	3,6-bis(diethylamino)-9-(o-chlorophenyl)xanthene	
	3,6-bis(diethylamino)-9-hexylxanthene	10
	3,6-bis(diethylamino)-9-(o-methoxycarbonylphenyl)xanthene	
	3,6-bis(diethylamino)-9-methylxanthene	
	3,6-bis(diethylamino)-9-phenylxanthene	
15	3,6-bis(diethylamino)-9-o-tolylxanthene	
	3,6-bis(dimethylamino)-9-(o-chlorophenyl)xanthene	15
	3,6-bis(dimethylamino)-9-ethylxanthene	
	3,6-bis(dimethylamino)-9-(o-methoxycarbonylphenyl)xanthene	
	3,6-bis(dimethylamino)-9-methylxanthene	
20	In addition to the above-listed aminoxanthenes the leuco forms of the xanthene dyes identified by the following Colour Index numbers may be used, 45000, 45005, 45010, 45015, 45050, 45070, 45090, 45095, 45100, 45105, 45150.	20
25	<b>c. Aminothioxanthenes</b>	
	3,6-bis(diethylamino)-9-(o-ethoxycarbonylphenyl)thioxanthene	
	3,6-bis(dimethylamino)-9-(o-methoxycarbonylphenyl)thioxanthene	
	3,6-bis(dimethylamino)thioxanthene	25
	3,6-dianilino-9-(o-ethoxycarbonylphenyl)thioxanthene	
30	<b>d. Amino-9,10-dihydroacridines</b>	
	3,6-bis(benzylamino)-9,10-dihydro-9-methylacridine	
	3,6-bis(diethylamino)-9-hexyl-9,10-dihydroacridine	
	3,6-bis(diethylamino)-9,10-dihydro-9-methylacridine	30
	3,6-bis(diethylamino)-9,10-dihydro-9-phenylacridine	
	3,6-diamino-9-hexyl-9,10-dihydroacridine	
	3,6-diamino-9,10-dihydro-9-methylacridine	
35	3,6-diamino-9,10-dihydro-9-phenylacridine	
	3,6-bis(dimethylamino)-9-hexyl-9,10-dihydroacridine	35
	3,6-bis(dimethylamino)-9,10-dihydro-9-methylacridine	
40	<b>e. Aminophenoazines</b>	40
	3,7-bis(diethylamino)phenoazine	
	9-dimethylamino-benzo[a]phenoazine	
	and the leuco forms of phenoazine dyes having CI numbers 51000, 51180, 51185, 51190, 51195.	
45	<b>f. Aminophothiazines</b>	45
	3,7-bis(benzylamino)phenothiazine and the leuco form of phenothiazine dyes having CI numbers 52000, 52010, 52015, 52020, 52025, 52030, 52035, 52050.	
50	<b>g. Aminodihydrophenazines</b>	
	3,7-bis(benzylethylamino)-5,10-dihydro-5-phenylphenazine	
	3,7-bis(diethylamino)-5-hexyl-5,10-dihydrophenazine	
	3,7-bis(dihexylamino)-5,10-dihydrophenazine	50
	3,7-bis(dimethylamino)-5-(p-chlorophenyl)-5,10-dihydrophenazine	
	3,7-diamino-5-(o-chlorophenyl)-5,10-dihydrophenazine	
	3,7-diamino-5,10-dihydrophenazine	
55	3,7-diamino-5,10-dihydro-5-methylphenazine	55

3,7-diamino-5-hexyl-5,10-dihydrophenazine  
 3,7-bis(dimethylamino)-5,10-dihydrophenazine  
 3,7-bis(dimethylamino)5,10-dihydro-5-phenylphenazine  
 3,7-bis(dimethylamino)5,10-dihydro-5-methylphenazine

5 Also included are the leuco forms of the phenazine dyes having CI numbers 50035, 50040, 50045, 50200, 50205, 5026, 50210, 50216, 50220, 50225, 50235, 50240.

h. *Aminodiphenylmethanes*

10	1,4-bis[ <i>bis-p</i> (diethylaminophenyl)methyl]piperazine <i>bis(p</i> -diethylaminophenyl) <i>anilinomethane</i> <i>bis(p</i> -diethylaminophenyl)-1-benzotriazolylmethane <i>bis(p</i> -diethylaminophenyl)-2-benzotriazolylmethane <i>bis(p</i> -diethylaminophenyl)( <i>p</i> -chloroanilino)methane <i>bis(p</i> -diethylaminophenyl)(2,4-dichloroanilino)methane <i>bis(p</i> -diethylaminophenyl)(methylamino)methane <i>bis(p</i> -diethylaminophenyl)(octadecylamino)methane <i>bis(p</i> -dimethylaminophenyl)aminomethane <i>bis(p</i> -dimethylaminophenyl) <i>anilinomethane</i>	10
15	<i>1,1-bis(dimethylaminophenyl)ethane</i> <i>1,1-bis(dimethylaminophenyl)heptane</i>	15
20	<i>bis(4-methylamino-m-tolyl)aminoethane</i> .	20

i. *Leuco indamines*

25	4-amino-4'-dimethylaminodiphenylamine <i>p</i> -( <i>p</i> -dimethylaminoanilino)phenol and the leuco forms of indamine and indophenol dyes having CI numbers 49400, 49405, 49410, 49700.	25
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j. *Aminohydrocinnamic acids, their esters, amides and cyanoethanes*

30	4-amino- $\alpha,\beta$ -dicyanohydrocinnamic acid, methyl ester <i>4-anilino-</i> $\alpha,\beta$ -dicyanohydrocinnamic acid, methyl ester <i>4-(p-chloroanilino)-</i> $\alpha,\beta$ -dicyanohydrocinnamic acid, methyl ester <i><math>\alpha</math>-cyano-4-dimethylaminohydrocinnamamide</i> <i><math>\alpha</math>-cyano-4-dimethylaminohydrocinnamic acid, methyl ester</i> <i><math>\alpha,\beta</math>-dicyano-4-diethylaminohydrocinnamic acid, methyl ester</i> <i><math>\alpha,\beta</math>-dicyano-4-dimethylaminohydrocinnamamide</i>	30
35	<i><math>\alpha,\beta</math>-dicyano-4-dimethylaminohydrocinnamic acid, methyl ester</i> <i><math>\alpha,\beta</math>-dicyano-4-dimethylaminohydrocinnamic acid</i> <i><math>\alpha,\beta</math>-dicyano-4-dimethylaminohydrocinnamic acid, hexyl ester</i> <i><math>\alpha,\beta</math>-dicyano-4-ethylaminohydrocinnamic acid, methyl ester</i> <i><math>\alpha,\beta</math>-dicyano-4-hexylaminohydrocinnamic acid, methyl ester</i> <i><math>\alpha,\beta</math>-dicyano-4-methylaminocinnamic acid, methyl ester</i>	35
40	<i>p-(2,2-dicyanoethyl)-N,N-dimethylaniline</i> <i>4-methoxy-4'-(1,2,2-tricyanoethyl)azobenzene</i> <i>4-(1,2,2-tricyanoethyl)azobenzene</i> <i>p-(1,2,2-tricyanoethyl)-N,N-dimethylaniline</i>	40

45 and substituted amino hydrocinnamic acids which are the leuco forms of dyes having CI numbers 48000, 48001, and 48005.

k. *Hydrazines*

50	1-( <i>p</i> -diethylaminophenyl)-2-(2-pyridyl)hydrazine <i>1-(p</i> -dimethylaminophenyl)-2-(2-pyridyl)hydrazine <i>1-(3-methyl-2-benzothiazolyl)-2-(4-hydroxy-1-naphthyl)hydrazine</i> <i>1-(2-naphthyl)-2-phenylhydrazine</i> <i>1-p-nitrophenyl-2-phenylhydrazine</i> <i>1 - (1,3,3 - trimethyl - 2 - indolinyl) - 2 - (3 - N - phenylcarbamoyl - 4 - hydroxy-1-naphthyl)hydrazine.</i>	50
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*l. Leuco indigoid dyes*

The leuco forms of indigoid dyes having CI numbers 73000, 73015, 73025, 73030, 73035, 73040, 73045, 73050, 73055, 73060, 73065, 73070, 73085, 73090, 73110, 73300, 73305, 73310, 73315, 73320, 73325, 73335, 73340, 73345, 73350, 73360.

5

*m. Amino-2,3-dihydroanthraquinones*

1,4-dianilino-2,3-dihydroanthraquinone  
1,4-bis(ethylamino)-2,3-dihydroanthraquinone

and leuco forms of dyes bearing CI numbers 61100, 61105, 61107, 61116, 61120, 61140, 61500, 61505, 61510, 61515, 61520, 61525, 61530, 61535, 61540, 61545, 61565, 61650.

10

*p. Arylethylanilines*

N-(2-cyanoethyl)-p-phenethylaniline  
N,N-diethyl-p-phenethylaniline  
15 N,N-dimethyl-p-[p-(1-naphthyl)ethyl]aniline  
N,N-dimethyl-p-[2-(4-nitro-1-naphthyl)ethyl]aniline  
N,N-dimethyl-p-phenethylaniline  
N,N-dimethyl-p-[2-(4-methoxy-1-naphthyl)ethyl]aniline  
p-(p-methoxyphenethyl)aniline  
20 p-[2-(1-naphthyl)ethyl]aniline  
p-(p-nitrophenethyl)aniline  
p-phenethylaniline

15

*2. Dimers of 2,4,5-triarylimidazolyl radicals.*

By triarylimidazolyl radicals are meant those containing aryl groups derived from both carbocyclic and heterocyclic aromatic compounds. Such aryl groups include phenyl, tolyl, xylyl, naphthyl and thiaryl groups. The aryl groups may be alike or different. Representative dimers of the imidazolyl radicals other than those given in the examples which fall within the scope of the invention are listed below, in terms of the substituents of the aryl groups when aryl is phenyl and in terms of other aryl groups than phenyl, by way of illustrating the light-activated imidazolyl dimers which may be employed in the composition.

25

I. Phenyl substituted imidazolyl radicals  
Substituents of phenyl rings attached at

2-Position	4-Position	5-Position
—	—	—
p-acetamido	p-methoxy	p-methoxy
o-acetoxy	—	—
p-amino	p-methoxy	p-methoxy
o-benzyl	—	—
o-benzylthio	o-benzylthio	o-benzylthio
p-[4,5-bis(p-methoxy-phenyl)-2-imidazolyl]	—	—
o-bromo	p-bromo	—
o-bromo	o-methoxy	o-methoxy
2-bromo-4-phenyl	—	—
o-butoxy	—	—

2-Position	4-Position	5-Position
o-t-butoxy	—	—
p-t-butoxy	—	—
p-t-butoxy	p-t-butoxy	p-t-butoxy
p-t-butoxy	o-butyl	—
o-t-butyl	—	—
o-t-butyl	p-t-butyl	p-t-butyl
N-butylacetamido	—	—
o-butylthio	—	—
p-t-butylthio	—	—
o-butyryloxy	—	—
o-chloro	—	—
o-chloro	o-chloro	o-chloro
o-chloro	p-chloro	—
o-chloro	p-chloro	p-chloro
o-chloro	3,4-dichloro	—
o-chloro	m-pentyloxy	—
o-chloro	m-pentyloxy	m-pentyloxy
o-chloro	p-propionyloxy	—
2-chloro-4-phenyl	—	—
p-chloro	p-chloro	p-chloro
o-cyano	—	—
o-cyano	p-t-butyl	—
o-cyano	p-t-butyl	p-t-butyl
o-cyano	p-cyano	p-cyano
o-cyano	p-methoxy	p-methoxy
2,3-dibromo	—	—
2,4-dibromo	—	—
2,6-dibutyl	—	—
2,4-di-t-butyl	—	—
2,4-di-t-butyl	2,4-difluoro	—
2,4-di-t-butyl	p-fluoro	p-fluoro

2-Position	4-Position	5-Position
o-dibutylsulfamoyl	—	—
2,4-dichloro	o-bromo	—
3,4-dichloro	2,4-dimethoxy	—
2,4-dicyano	p-cyano	p-cyano
2,6-dicyano	—	—
3,5-dicyano-4-methoxy	—	—
p-(2,2-dicyanovinyl)	—	—
2,4-diethoxy	—	—
o-diethylsulfamoyl	—	—
2,5-difluoro	p-cyano	—
2,5-difluoro	p-cyano	p-cyano
2,4-dimethoxy	o-chloro	—
2,4-dimethoxy	o-chloro	o-chloro
2,4-dimethoxy	2,4-dimethoxy	—
2,4-dimethoxy	2,4-dimethoxy	2,4-dimethoxy
2,4-dimethoxy	o-methoxy	—
2,4-dimethoxy	p-methoxy	—
2,4-dimethoxy	p-methoxy	p-methoxy
2,4-dimethoxy	m-phenylthio	—
2,4-dimethoxy	m-phenylthio	m-phenylthio
3,4-dimethoxy	o-cyano	—
3,4-dimethoxy	2,4-dipentyl	2,4-dipentyl
o-dimethylamino	—	—
o-dimethylamino	p-dipentylamino	—
o-dimethylamino	o-dipropylsulfamoyl	—
p-dimethylamino	p-methoxy	p-methoxy
3-dimethylamino-4-methoxy	—	—
o-dimethylcarbamoyl	—	—
2,4-dipentyl	2,4-dipentyl	2,4-dipentyl
o-dipentylamino	—	—

2-Position	4-Position	5-Position
p-(4,5-diphenyl-2-imidazolyl)	—	—
p-[4-(4,5-diphenyl-2-imidazolyl)phenyl]	—	—
2,4-diproxy	—	—
2,4-dinaphthyl thio	—	—
2,4-diproxy	o-diethylcarbamoyl	—
o-dipropylcarbamoyl	—	—
p-ethoxy	—	—
p-ethoxy	p-diethylsulfamoyl	—
o-ethoxycarbonyl	—	—
o-ethyl	—	—
o-N-ethylbutyramido	—	—
o-N-ethylpropylamino	—	—
o-ethylthio	—	—
o-N-ethylvaleramido	p-t-pentyl	p-t-pentyl
o-fluoro	o-methoxy	o-methoxy
p-fluoro	2-bromo-4,5-di-tert.-butoxy	2-chloro-4-methoxy-3-methyl
p-hexyloxy	p-methoxycarbonyl	p-methoxycarbonyl
o-methoxy	—	—
o-methoxy	p-chloro	—
o-methoxy	o-methylthio	o-methylthio
o-methoxy	p-nitro	—
o-methoxy	p-nitro	—
o-methoxy	p-phenylsulfonyl	—
o-methoxy	p-phenylsulfonyl	p-phenylsulfonyl
p-methoxy	p-benzylthio	p-benzylthio
p-methoxy	m-butyryloxy	m-butyryloxy
p-methoxy	2-chloro-4,5-dimethoxy	2-chloro-4,5-dimethoxy
p-methoxy	m-dimethyl-carbamoyl	—
o-methoxycarbonyl	p-N-ethylphenyl	—

2-Position	4-Position	5-Position
o-methoxycarbonyl	sulfamoyl	—
p-methoxycarbonyl	—	—
4-methoxy-3-nitro	—	—
2-methoxy-4-phenyl	—	—
o-methyl	p-benzoyloxy	p-benzoyloxy
o-methyl	o-methyl	o-methyl
m-N-methylacetamido	p-methoxy	p-methoxy
o-N-methylacetamido	o-N-ethylbutyramido	o-N-ethylbutyramido
o-N-methylacetamido	o-N-methylacetamido	—
o-N-methylacetamido	o-N-methylacetamido	o-N-methylacetamido
o-N-methylpropion-amido	—	—
o-methylthio	—	—
p-methylthio	p-methoxy	p-methoxy
p-methylthio	p-methylthio	—
p-methylthio	p-methylthio	p-methylthio
o-1-naphthyl	p-phenoxy	—
o-2-naphthyl	—	—
m-nitro	2,4-dimethoxy	2,4-dimethoxy
m-nitro	2,4-dimethylthio	—
o-t-pentyl	—	—
p-pentyl	—	—
o-pentyloxy	—	—
p-pentyloxy	—	—
o-pentyloxycarbonyl	—	—
o-phenoxy	—	—
o-phenoxy	3,4,5-trimethoxy	3,4,5-trimethoxy
p-phenoxy	p-methoxy	—
m-phenyl	p-phenyl	p-phenyl
o-phenyl	—	—
o-phenyl	p-methoxycarbonyl	p-methoxycarbonyl

2-Position	4-Position	5-Position
o-phenyl	m-pentyloxycarbonyl	—
o-phenyl	m-pentyloxycarbonyl	m-pentyloxycarbonyl
o-phenyl	p-phenyl	p-phenyl
p-phenyl	p-phenyl	p-phenyl
p-phenylhydrazinomethyl	—	—
o-phenylthio	p-1-naphthylthio	p-1-naphthylthio
p-phenylthio	p-methoxy	p-methoxy
o-propoxy	—	—
2,4,6-tribromo	—	—
2,4,6-tributyl	—	—
2,4,6-tri-t-butyl	—	—
2,3,5-trichloro	—	—
2,4,6-trichloro	—	—
2,4,6-trichloro	o-butylthio	—
2,4,6-tricyano	p-cyano	p-cyano
2,4,6-triethoxy	—	—
p-trifluoromethoxy	—	—
2,3,4-trimethoxy	—	—
2,4,6-trimethoxy	—	—
3,4,5-trimethoxy	—	—
3,4,5-trimethyl	3,4,5-trimethyl	3,4,5-trimethyl
2,4,6-tri-t-pentyl	—	—
2,4,6-tripropoxy	—	—
—	o-t-butoxy	—
—	p-butoxy	—
—	4-t-butoxy-2-methoxy	—
—	p-t-butyl	—
—	p-t-butylthio	p-t-butylthio
—	o-chloro	2,5-dimethoxy
—	2-chloro-4-methoxy	—

2-Position	4-Position	5-Position
—	2-cyano-2,4-dimethoxy	—
—	2,4-di-t-butoxy	—
—	2,3-dichloro	2,4-dimethylthio
—	2,4-dimethoxy	—
—	2,4-dimethoxy	2,4,5-trimethoxy
—	2,5-dimethyl	2,5-dimethyl
—	2,5-dipentyl	—
—	o-methoxy	o-methoxy
—	o-methoxy	p-methoxy
—	4-methoxy-3-nitro-	2-methoxy-4-methyl
—	o-methyl	2,4,5-trimethoxy
—	p-methyl	—
—	p-methylthio	—
—	p-methylthio	p-methylthio
—	p-pentyl	—
—	p-t-pentyloxy	p-t-pentyloxy
—	2,4,5-trimethoxy	p-methoxy
—	2,4,5-trimethyl	—

## II Other ring groups than phenyl in imidazolyl radical

2-Position	4-Position	5-Position
2,4-dipentylphenyl	2-naphthyl	2-naphthyl
p-methoxyphenyl	2-naphthyl	2-naphthyl
o-methoxycarbonyl phenyl	2-naphthyl	phenyl
(1-methoxy-2-naphthyl)	phenyl	phenyl
(3-methoxy-2-naphthyl)	phenyl	phenyl
1-naphthyl	phenyl	phenyl
o-pentyloxycarbonyl-phenyl	2-naphthyl	2-naphthyl

The above dimers of 2,4,5-triarylimidazolyl radicals which provide light-activated components for the invention compositions are characterized by the property of dissociating into two triarylimidazolyl free radicals when illuminated with ultraviolet light of the aforementioned wave length. Such a dissociation may be detected, and the existence of the free radicals discerned, by electron paramagnetic resonance, by ultraviolet spectra, and by visible spectra.

The triarylimidazoles which are intermediates for the biimidazoles or dimers of the 2,4,5-triarylimidazolyl radicals may suitably be prepared as follows:

(A) By refluxing, in glacial acetic acid containing ammonium acetate; benzil, binaphthoyl, naphthylphenylglyoxal, or an appropriately substituted compound of the benzil type with an aromatic aldehyde such as benzaldehyde, a naphthaldehyde, a phenanthraldehyde or with picolinaldehyde, a nicotinaldehyde, a thiophenealdehyde or a substituted aromatic aldehyde. The reaction product is precipitated by drowning the reaction mass, e.g., in water or in an ammonium hydroxide solution, and is recovered by filtration. The product can then be purified by recrystallization from a solvent. This procedure is described by Davidson et al, J. Org. Chem. 2, 319 (1937).

(B) By refluxing a benzoin and one of the abovementioned aromatic aldehydes in methanol in the presence of copper acetate and ammonia. This is an adaptation of the procedure of Wiedenhagen et al, Ber. 70, 570 (1937).

(C) By heating a benzil or one of the above-named compounds of the benzil type with an aforementioned aromatic aldehyde at 180° to 190°C. in formamide solution as disclosed in Belgian Patent Specification No. 589,417.

The intermediate triarylimidazole is dissolved in ethanol containing potassium hydroxide and then oxidized to the corresponding biimidazole or dimer of the triarylimidazolyl radical by treatment with aqueous potassium ferricyanide. The desired product precipitates from the reaction mixture, is isolated by filtration, and is washed free from ferricyanide with water. This procedure is described by Hayashi et al., Bull. Chem. Soc. Japan, 33, 565 (1960). The triarylimidazole may also be oxidized by agitating a benzene or chloroform solution of the imidazole with lead dioxide ( $PbO_2$ ) or by passing a saturated solution of the imidazole in benzene through a column packed with  $PbO_2$  and diatomaceous earth.

These triarylimidazolyl dimers exist in various isomeric forms which differ from one another in the position of the covalent bond joining the two radicals and in the position of the double bonds in the radicals, the position of one being fixed by the position of the other. For example, when the one end of the linkage is at a 1 position in one of the radicals, the double bond in that radical is in the 2,3 and 4,5 positions and when one end of the linkage is at a 2 position the double bonds in that radical occur in the 3,4 and 5,1 positions. Naturally, the linkage may go to different positions in each radical. For example, it may be between the 1,2' or 1,4' positions as well as between similar positions such as the 1,1' or 2,2' positions. The various isomers exhibit differing spectral and thermotropic properties.

The preferred 2,4,5-triarylimidazolyl dimers are 2,2',4,4',5,5'-hexaphenylbiimidazoles having in the 2- and 2'-phenyl rings an ortho substituent that is chlorine, bromine, fluorine, methoxy, or methyl. Such a dimer has less tendency than other differently substituted dimers to form color during the drying of the light-sensitive composition on substrates at somewhat elevated temperatures, for instance, in the range of 70° to 100°C.

The biimidazoles used in the present invention are phototropic, i.e., they change color upon exposure to ultraviolet radiation and return to their original color after the light source is removed. They may by virtue of this property contribute some color to the image that is produced when a leuco dye composition containing a biimidazole is irradiated. This color is, however, fugitive. It fades at varying rates depending upon the substituent group in the biimidazole, and is not relied upon to color the image produced by radiation. The leuco dye component provides the permanent colored image when reacted upon by the free radicals of the biimidazole when the biimidazole is activated by ultraviolet light. The primary purpose of the biimidazole, then, is to furnish a photosensitive material which, upon radiation, is activated to react with the leuco dye to develop color in accordance with the pattern of an irradiated area.

The leuco form of the dye and the dimer of the 2,4,5-triarylimidazolyl radical may be mixed in mole ratios within the range from 10:1 (leuco dye : dimer) to 1:10. When intimately mixed, preferably by means of a small quantity of solvent, such mixtures will produce on substrates a permanent image when irradiated with ultraviolet light. The preferred ratio range is 2:1 to 1:2, while the preferred ratio is 1:1.

*3. Acids for leuco dye salt formation.*

With the leuco form of dyes which have amino or substituted amino groups within the dye structure and which are characterized as cationic dyes, an amine salt-forming mineral acid, organic acid, or an acid from a compound supplying acid may be employed. The amount of acid may vary from 0.33 mole to 1 mole per mole of amino nitrogen in the dye. The preferred quantity of acid is 1 mole per mole of amino nitrogen. Acid in an amount in excess of that required to form a salt with the amino nitrogen should be avoided because excess acid reduces the reactivity of the light-activated biimidazole and renders the composition less light-sensitive. Representative acids which form the required amine salts are hydrochloric, hydrobromic, sulfuric, nitric, phosphoric, acetic, oxalic, and p-toluenesulfonic acid. Other acids such as acids in the "Lewis" sense or acid sources which may be employed in the presence of water or moisture include zinc chloride, zinc bromide, and ferric chloride. Representative salts include, for example, the hydrochloride and zinc chloride salt of tris(o-methyl-p-diethylaminophenyl)methane three and one acid molecules per molecule of leuco dye respectively) and the oxalic acid salt of the same leuco dye (three molecules of acid per molecule of leuco dye).

With the leuco form of dyes which produce dyes by the removal of two hydrogen atoms, acid is not needed and in most cases should be avoided to prevent desensitizing the light-sensitive composition.

*4. Solvents.*

Solvents which are inert toward the leuco form of the dye and the dimer of the triarylimidazolyl radical are usually employed to dissolve these components and thereby mix them together and to provide a fluid medium for a convenient and ready application of the light-sensitive composition to substrates such as paper. Also a small residue of solvent in the dried composition is found to be essential for the production of an image upon radiation; an exhaustively dried composition does not respond to ultraviolet light to produce an image. That light-sensitivity which is lost by complete drying is restored, however, by introducing a small amount of solvent as by spraying, brushing and dipping.

The requirement that "solvent" be present in the substrate, paper for instance, is not meant to convey the idea that the paper must necessarily be wet, humidified, or otherwise specially moistened. Numerous solvents such as N,N-dimethylformamide, N,N-diethylacetamide, and dimethylsulfoxide are so strongly adsorbed by cellulosic and plastic substrates that prolonged heating under vacuum is necessary for complete solvent removal. Ordinary drying such as that employed in paper manufacture or in film casting results in the retention of ample solvent to give a composition with good photosensitivity. The compositions so produced are definitely dry to the touch and stable to storage at room temperature. Indeed moisture of the air is adsorbed by many of the compositions, particularly those comprising an acid salt of an amino leuco form of a dye on cellulosic substrates, and serves as a suitable solvent.

Some solvents such as methanol and ethanol may be removed from cellulosic materials readily and completely enough to reduce the photosensitivity of the composition to impractically low levels. When such combinations of solvents-substrates are employed, images are formed only when the substrate is wet to the touch. Such solvents are best used in applications which permit storage of the treated paper under conditions which prevent solvent evaporation. When it is practical to form an image on a wet substrate, solvents of this type may be used with the advantage that simple drying prevents color formation in uncolored areas. In general, a solvent should dissolve the leuco dye, biimidazole and binder, if employed, but be inert to the photo-sensitive materials.

In general, a preferred solvent has a boiling point of at least 60°C. at atmospheric pressure. Solvents with low vapor pressures and consequent high boiling points may be used. Their failure to be readily removed by evaporation will not present a problem, if the quantity used is restricted, as it readily can be in mixtures of solvents with relatively high vapor pressures. It is preferable to have at least 0.5% by weight of solvent retained by such a substrate as paper to ensure optimum image formation upon proper radiation. Among the solvents which have been and may be employed on paper are formamide, N,N-dimethylformamide, N,N-dimethylacetamide, hexanoamide, stearamide, methanol, ethanol, 1-propanol, 2-propanol, butanol, ethylene glycol, polyethylene glycols, ethyl acetate, ethylbenzoate, benzene, o-dichlorobenzene, toluene, dimethylsulfoxide, pyridine, tetrahydrofuran, dioxane, dicyanocyclobutane, 1-methyl-2-oxohexamethyleneimine, and mixture of these solvents in various proportions as may be

required to attain solution of the particular leuco dye and biimidazole selected for use in a composition.

5. *Binders.*

In addition to a residual amount of a solvent a binder may be present in the light-sensitive composition spread over a substrate. Binders which may optionally be added to the composition are inert materials that serve to adhere the leuco dye-biimidazole mixture to a substrate. The binder may also serve to thicken the solution of the composition should this be desirable for specific applications. Representative binders that will be found applicable are ethyl cellulose, polyvinyl alcohol, polyvinylchloride, polystyrene, polyvinyl acetate, polymethylmethacrylate, cellulose acetate, cellulose nitrate, chlorinated rubber, polymers and copolymers of vinyl monomers and gelatin. A binder will be used in an amount varying from 0.5 part to 10 parts by weight per part of combined weight of leuco dye and biimidazole.

6. *Substrates.*

The substrates are materials which bear the lightsensitive, image-forming compositions as a coating or impregnant. They are materials commonly used in the graphic arts and in decorative applications. These materials include paper ranging from tissue paper to heavy cardboard; films of plastics and polymeric materials such as regenerated cellulose, cellulose acetate, cellulose nitrate, polyester of glycol and terephthalic acid, vinyl polymers and copolymers, polyethylene, polyvinylacetate, polymethyl methacrylate, polyvinylchloride; textile fabrics; glass; wood and metals. Opaque as well as transparent substrates can be used. Substrates in which the photosensitive components are dissolved or which bear the photosensitive components as a coating on the reverse side of the substrate, i.e. on the side away from the ultraviolet light source used for image formation, must be transparent not only in the visible region but transparent to a portion of the ultraviolet range useful for image formation. The substrates must also be inert to the photosensitive materials and preferably should not dissolve the active components but adsorb them and retain sufficient solvent to provide a medium for rapid image formation upon irradiation. Reactive resins, drying oil, and other agents which may adversely affect image formation by the photosensitive composition are to be avoided.

7. *Preparation of compositions.*

A common procedure is to make a solution of a leuco dye ranging in concentration from 0.5% by weight to the limit of the solubility of the compounds in a solvent comprising, for instance, 50:50 by volume of N,N-dimethylformamide and benzene, and to add to this solution a dimer of a 2,4,5-triarylimidazolyl radical in an amount equivalent on a molar basis to the leuco dye. Optionally, a binder such as polyvinyl alcohol may be added to the solution. The selection of the leuco dye will depend upon the color and quality of the image desired. Two or more leuco dyes may be used in admixture to obtain a particular color or shade of color or to provide a neutral gray or black coloration in the image.

In applying a solution to paper, films, fabrics, or to the surfaces of rigid substrates such as glass, wood or metals the solution may be sprayed, brushed, applied by a roller or an immersion coater, flowed over the surface, picked up by immersion or spread by other means. Complete coverage of the substrate may be attained or a pattern of the light-sensitive composition may be printed on the substrate. In impregnating paper, for instance, such concentrations of solution and pick-up by the paper are made so as to provide from 0.01 mg. in.<sup>2</sup> to 5.0 mg./in.<sup>2</sup> of leuco dye and the equivalent amount of biimidazole activator (equimolecular amounts of leuco dye and biimidazole activator). Images of greater and lesser intensity of color are provided by the application of greater and lesser amounts of leuco dye to the substrate.

The substrates bearing the solution of the leuco dye and biimidazole, and optionally a binder, may be dried simply at room temperature. They also may be dried under vacuum at room temperature or at elevated temperatures. The upper temperature limit is critical in combination with exposure time. A short exposure to heat of 90°C. may not be detectably harmful, while several hours' exposure to this heat will reduce the light sensitivity of the composition. The deposits of light-sensitive compositions remaining on the substrate are in most cases colorless and in all cases subject to a distinct color development or color change upon irradiation with ultraviolet light.

8. *Light sources and image formation.*

Any convenient source of ultraviolet light may be used to activate the light-sensitive composition and induce the formation of an image. Among the light sources which have been employed are a sun lamp, an electronic flash gun, a germicidal lamp, ultraviolet lamps providing specifically light of short wave length (2537 Å) and lamps providing light of long wave length (3663 Å). The light exposure time will vary from a fraction of a second to several minutes depending upon the intensity of the light, its distance from the light-sensitive composition, the nature and amount of the light-sensitive composition available, and the intensity of color in the image desired. In general, light sources that supply radiation in the region between about 2000 Å and about 4200 Å are useful in producing images with the leuco dye-hexaarylbiimidazole-solvent compositions on numerous substrates.

Images may be formed by a beam of light or by exposure to light of a selected area behind a negative, a stencil, or other relatively opaque pattern. The negative may be a silver negative with cellulose acetate or polyester film. The negative may also be one in which the opacity results from aggregations of areas of different refractive index. Image formation may also be accomplished in conventional diazo printing apparatus, or in a thermography device, provided the instrument emits some of its light in the ultraviolet range. A piece of onionskin paper which bears typewriting, for example, will serve as a master pattern from which copies can be made.

9. *Fixing treatment.*

In order to retain an image once it has been formed, color development in the unilluminated portions of the image pattern by exposure to ultraviolet light must be avoided. One way the original image is preserved is to apply to the imaged material, e.g., paper, film, fabric or whatever the substrate, by spraying or by immersion, a solution of a strong hydrogen absorber not leading to colored products, e.g. hydroquinone. Hydroquinone is more susceptible to hydrogen abstraction than is the leuco dye, and it preferentially reacts with any activated biimidazole without color formation. Printed compositions so "fixed" with hydroquinone having a lasting quality and are little or not at all affected by any subsequent ultraviolet light exposure. The image itself will of course, be subject to color change in accordance with the fastness to light of the particular dye employed.

Another fixing treatment consists of washing with water the unreacted leuco dye, after an image has been formed, from the material to which the light-sensitive composition has been applied.

The novel light-sensitive compositions of the present invention are useful in a variety of applications. Among these are:

(1) *Radiation dosimeters.* These compositions may be used as papers to determine easily the quantity of solar radiation that falls on a particular surface. It may also be useful to employ these as low cost light-meters in photographic applications. For these uses, it is necessary to compare areas which have been exposed to previously calibrated papers or surfaces, in order to allow easy analysis of the degree of radiation.

(2) *Printing applications.* Very soft paper, as for example, tissue paper, can be easily imaged when it has been treated with these compositions, by projecting an image onto the treated surface. Subsequently, the image may be fixed by a variety of methods, including washing out of the unreacted leuco dyes by simple treatment with water. These soft tissue paper materials cannot be readily imaged by conventional printing techniques.

(3) *Blue prints.* These light-sensitive compositions can find application in diazo printout equipment, where they can be made to give readily a variety of shades, with different speeds and sensitivities. It is possible to utilize these materials with caution in ordinary room light, rather than have to handle them in the dark.

This invention makes available a process for forming an image in continuous tone, by a dry, rapid, readily controllable procedure.

In order that the invention may be more fully understood the following Examples are given by way of illustration only.

EXAMPLE 1.

Tris (4-diethylamino-o-tolyl)methane trihydrochloride in an amount of 0.5 g. and 0.5 g. of 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetraphenylbiimidazole are dissolved in 100 ml. of a solution of equal parts by volume of benzene and N,N-dimethylformamide. The resultant solution is used to impregnate 1000 square inches of filter paper, and the paper is dried at 40°C. for half an hour in a blower oven. The treated

paper is colorless. When a strip of it is partly covered and exposed to the light of a photographic flash gun for 0.001 sec. the uncovered area turns an intense blue color. Similarly, another strip of the treated paper exposed to direct sunlight for 5 sec. becomes blue.

5 Color also develops, but to a less intense degree, when paper is treated with 0.1 of the above concentration of leuco dye and biimidazole and exposed to both these sources of ultraviolet light.

When cotton fabric is immersed in the above leuco dye-biimidazole solutions and similarly dried it is rendered photosensitive and undergoes blue coloration on exposure 10 to the ultraviolet light.

10 When the 0.5% by weight solution of each of the above leuco dye and biimidazole is sprayed onto tissue paper, the paper becomes photosensitive and blue coloring appears on exposure to sunlight where contact with the solution occurs.

15 To 100 parts by volume of the benzene-dimethylformamide solution containing 0.5 part by weight each of the above leuco dye and biimidazole is added 0.25 part by weight of ethyl cellulose. This solution is used to impregnate and coat filter paper, bond paper, sized paper, and cardboard. The various papers dried in the oven at 40°C. are colorless, photosensitive specimens until irradiated and then they present a blue coloration. A portion of this same solution is also used to coat anodized aluminum, 20 glass, and a polyester film. Evaporation of the solvent leaves an adherent coating of a photosensitive composition on each of these substrates. A blue color forms in the surface film upon exposure to ultraviolet light.

20 When the bis(o-chlorophenyl)tetraphenylbiimidazole in the above solution is replaced with 2,2',4,4',5,5'-hexaphenylbiimidazole a photosensitive composition is formed that can be similarly applied to paper and other substrates for the development 25 of blue color upon illumination with ultraviolet light.

#### EXAMPLE 2.

30 Bis(4-dimethylamino-o-tolyl)phenylmethane dihydrochloride is used in place of the leuco dye of Example 1 in the 0.5% solution, and the solution is used to impregnate paper as described in the previous example. The resultant composition produces an intense green color when exposed to ultraviolet light. A less intense but definitely discernable coloration is obtained when 0.1 of this concentration of this leuco dye and biimidazole sensitizer is used in preparing the photosensitive paper specimens.

#### EXAMPLE 3.

35 When the leuco dye in the solution of the first part of Example 1 comprises 0.25 g. each of the leuco dyes of Example 1 and Example 2 the photosensitive composition produces a blue-green color when irradiated on paper. By varying the proportions of these leuco dyes various blue-green shades ranging from blue to green are obtained.

#### EXAMPLE 4.

40 When 0.25 g. each of the leuco dye of Example 1 and of Example 2 and of 4,4'-dihydroxy-3,3',5,5'-tetrabromobiphenyl taken in admixture compose the leuco dye in the solution of Example 1 and paper is rendered photosensitive with this composition, a brown color develops upon exposure to ultraviolet light. When three times this concentration of each of the same leuco dyes is employed, the color formed on the paper 45 by illumination is black.

#### EXAMPLE 5.

50 A permanent image is formed by the following procedure: A sheet of paper is briefly immersed in a solution of equal parts of benzene and N,N-dimethylformamide containing 0.5% each of tris(4-diethylamino-o-tolyl)methane trihydrochloride and 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetraphenylbiimidazole. The impregnated paper is dried at 80°C. for two minutes. The paper then illuminated with the light from a photographic flashgun through a photographic film negative bears a distinct, clear image in blue color. The exposed, printed paper is now immersed in a saturated ether solution of hydroquinone for about 10 seconds, removed, and allowed to dry. The image is thus "fixed" and is unaltered by further exposure to light; the treatment with hydroquinone has prevented further color formation.

55 Herewith follows a series of examples of various leuco dyes which are used at a concentration of 0.5% in admixture with 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetraphenylbiimidazole with a concentration of 0.5% in a 50:50 benzene-N,N-dimethylformamide solution to provide a composition for photosensitizing paper as described in Example 1. The color of the image produced on exposure to ultraviolet light is given together with the particular leuco form of the dye present in a composition.

Ex. No.	Leuco Dye	Color of Light- Induced Image
6	Tris (p-hydroxyphenyl)methane	Red
7	Bis (4-diethylamino-o-tolyl)phenylmethane dihydrochloride*	Green
8	Double zinc chloride salt of 3,6-bis (di-ethylamino)-9-(o-ethoxycarbonylphenyl)-xanthene	Red
9	Double zinc chloride salt of 9,10-dihydro-3,6-bis (dimethylamino)-9-phenylacridine	Red
10	Zinc chloride salt of 9-dimethylamino-benzo-[ $\alpha$ ]-phenoxazine	Blue
11	Double zinc chloride salt of 3,7-bis(dimethylamino)phenothiazine	Blue
12	Phenothiazine	Blue-green
13	Zinc chloride salt of 5,10-dihydro-3,7-bis(dimethylamino)-5-phenylphenazine	Blue
14	Bis(p-dimethylaminophenyl)piperidinomethane	Blue
15	4-amino-4'-dimethylaminodiphenylamine	Blue
16	p-(p-Dimethylaminoanilino)phenol	Blue
17	p-(2,2-Dicyanoethyl)-N,N-dimethylaniline	Yellow
18	p-(1,2,2-Tricyanoethyl)-N,N-dimethylaniline	Orange
19	$\alpha,\beta$ -Dicyano-4-diethylaminohydrocinnamic acid, methyl ester *	Orange
20	1-p-Dimethylaminophenyl-2-p-nitrophenyl hydrazine	Orange
21	Leuco thioindigo	Red
22	2,3-Dihydro-1,4-bis-(methylamino)anthraquinone	Blue
23	3,3',5,5'-Tetrabromo-p,p-biphenol	Orange
24	2-(p-Hydroxyphenyl)-4,5-diphenylimidazole	Red
25	p-Phenylenediamine	Gray

\* The solvent employed in this example was an 85/15 mixture of N,N-dimethylformamide/methanol.

In another series of examples, dimers of various 2,4,5-triarylimidazole radicals are used at a concentration of 0.15% in admixture with tris(4-diethylamino-o-tolyl)-methane trihydrochloride at a concentration of 0.15% in a 50:50 benzene-N,N-dimethylformamide solution to provide a composition for photosensitizing paper as described in Example 1. The particular imidazolyl radical, which composed the biimidazole present in admixture with the leuco dye, and the color of the image produced on exposure to ultraviolet light are given in the following table.

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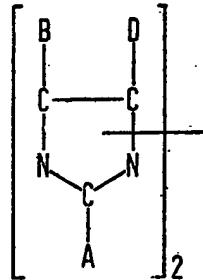
Ex. No.	Imidazolyl radical of dimer in composition	Color of light- Induced Image
26	2-(p-benzylthiophenyl)-4,5-diphenyl	Blue
27	4,5-bis(p-benzylthiophenyl)-2-phenyl	Blue
28	2,4,5-tris(p-benzylthiophenyl)	Green
29	2-(m-bromophenyl)-4,5-diphenyl	Blue
30	2-(o-bromophenyl)-4,5-diphenyl	Blue
31	2-(p-bromophenyl)-4,5-diphenyl	Blue
32	2-(bromophenyl)4,5-bis(p-methoxyphenyl)	Blue
33	2-(p-carboxyphenyl)-4,5-diphenyl	Blue
34	2-(m-chlorophenyl)-4,5-diphenyl	Blue
35	2-(m-chlorophenyl)-4,5-bis(p-methoxyphenyl)	Blue
36	2-(o-chlorophenyl)-4,5-bis(p-methoxyphenyl)	Blue
37	2-(o-chlorophenyl)-4-(1-naphthyl)-5-phenyl	Blue
38	2-(p-chlorophenyl)-4,5-diphenyl	Blue
39	2-(p-chlorophenyl)-4,5-bis(p-methoxyphenyl)	Blue
40	2-(2,4-dichlorophenyl)-4,5-diphenyl	Blue
41	4-(o-chlorophenyl)-2,5-diphenyl	Blue
42	4,5-bis(o-chlorophenyl)-2-phenyl	Blue
43	2-(p-cyanophenyl)4,5-diphenyl	Blue
44	2-(cyanophenyl)-4,5-bis(p-methoxyphenyl)	Green
45	2-(o-ethoxyphenyl)-4,5-diphenyl	Blue
46	2-(p-iodophenyl)-4,5-diphenyl	Blue
47	2-(m-fluorophenyl)-4,5-diphenyl	Blue
48	2-(o-fluorophenyl)-4,5-diphenyl	Blue
49	2-(p-fluorophenyl)-4,5-diphenyl	Blue
50	2-(4-trifluoromethoxyphenyl)-4,5-diphenyl	Blue
51	2-(p-trifluoromethylsulfonylphenyl)-4,5-diphenyl	Blue

Ex. No.	Imidazolyl radical of dimer in composition	Color of light- Induced Image
52	2-(o-methoxyphenyl)-4,5-bis(p-methoxyphenyl)	Blue
53	2-(p-methoxyphenyl)-4,5-diphenyl	Blue
54	2-(p-methoxyphenyl)-4-(o-methoxyphenyl)-5-phenyl	Blue
55	2-(p-methoxyphenyl)-4,5-bis(o-methoxyphenyl)	Blue
56	4-(o-methoxyphenyl)-2,5-diphenyl	Blue
57	4-(p-methoxyphenyl)-2,5-diphenyl	Blue
58	2-(o-methoxyphenyl)-4-(p-methoxyphenyl)-5-phenyl	Blue
59	2,4-bis(o-methoxyphenyl)-5-phenyl	Blue
60	2,4-bis(o-methoxyphenyl)-5-phenyl	Green-Blue
61	4,5-bis(p-methoxyphenyl)-2-(2,4-dichlorophenyl)	Blue
62	4,5-bis(p-methoxyphenyl)-2-(1-naphthyl)	Blue
63	4,5-bis(p-methoxyphenyl)-2-phenyl	Blue
64	2,4,5-tris(o-methoxyphenyl)	Blue
65	2,4,5-tris(p-methoxyphenyl)	Green-Blue
66	2-(2,3-dimethoxyphenyl)-4,5-diphenyl	Blue
67	2-(2,4-dimethoxyphenyl)-4,5-diphenyl	Green-Blue
68	2-(3,4-dimethoxyphenyl)-4,5-diphenyl	Green-Blue
69	2-(2,4,6-trimethylphenyl)-4,5-diphenyl	Blue
70	2-(3,4-methylenedioxyphenyl)-4,5-diphenyl	Green-Blue
71	2-(p-methylthiophenyl)-4,5-diphenyl	Blue
72	2-(1-naphthyl)-4,5-diphenyl	Blue
73	4-(1-naphthyl)-2,5-diphenyl	Blue
74	2,4-di(1-naphthyl)-5-phenyl	Blue
75	4,5-di-(1-naphthyl)-2-phenyl	Blue
76	2,4,5-tri(1-naphthyl)	Blue
77	2-(2-naphthyl)-4,5-diphenyl	Blue
78	2-(m-nitrophenyl)-4,5-diphenyl	Blue
79	2-(p-nitrophenyl)-4,5-diphenyl	Green
80	2-(p-nitrophenyl)-4,5-bis(p-methoxyphenyl)	Green
81	2-(4-chloro-1-naphthyl)-4,5-diphenyl	Blue

Ex. No.	Imidazolyl radical of dimer in composition	Color of light- Induced Image
82	2-(p-phenylsulfonylphenyl)-4,5-diphenyl	Blue
83	4,5-diphenyl-2-(p-sulfamoylphenyl)	Blue
84	4,5-diphenyl-2-(2-thienyl)	Green
85	4,5-diphenyl-2-(o-tolyl)	Blue
86	2,5-diphenyl-4-(o-tolyl)	Blue
87	2-phenyl-4,5-(o-tolyl)	Blue
88	5-phenyl-4-(o-tolyl)-2-(p-tolyl)	Blue
89	4,5-diphenyl-2-(p-tolyl)	Blue
90	2-phenyl-4,5-di(2,4-xylyl)	Blue
91	4,5-di-(o-tolyl)-2-(p-tolyl)	Blue

## WHAT WE CLAIM IS:—

1. A composition which comprises an admixture of (1) a dye in the leuco form having the formula  $DH_n$  where H is a hydrogen atom whose removal forms a compound colored differently to  $DH_n$  and n is 1 or 2 and (2) a 1,2,5-triarylimidazolyl dimer consisting of two imidazolyl units joined together by a single covalent bond, the dimer having the formula:—



wherein the valences of the atoms in the imidazolyl rings, other than those through which the imidazolyl rings are joined, are satisfied by two conjugated intracyclic double bonds, and where A, B and D, which may be the same or different, are substituted or unsubstituted carbocyclic or heterocyclic aromatic radicals, the dimer being dissociated into free radicals when irradiated with ultraviolet light.

2. A composition according to Claim 1 wherein  $DH_n$  is an acid addition salt of the leuco form of a triphenylmethane dye having in at least two of the phenyl rings and positioned para to the methane carbon atom an amino, alkylamino (containing from 1 to 4 carbon atoms) or a dialkylamino (containing from 1 to 4 carbon atoms in each alkyl group) substituent group and the 2,4,5-triarylimidazolyl dimer is the dimer of either (a) the 2,4,5-triarylimidazolyl radical having an ortho substituent in the 2-phenyl and 2'-phenyl rings selected from chlorine, bromine or, fluorine atoms or a methoxy group or an alkyl group containing from 1 to 4 carbon atoms or (b) the 2-(1-naphthyl)-4,5-diphenylimidazolyl radical.

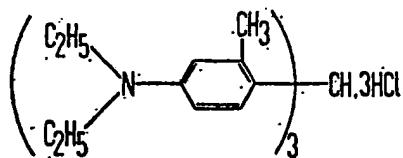
3. A composition according to Claim 1 in which  $DH_n$  is

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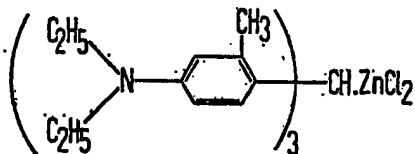
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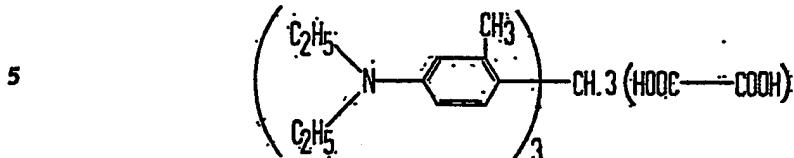
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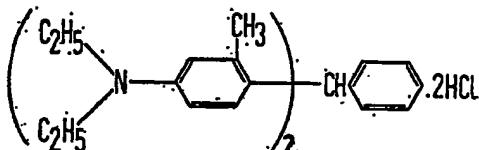
4. A composition according to Claim 1 in which DH<sub>a</sub> is



5. A composition according to Claim 1 in which DH<sub>a</sub> is



6. A composition according to Claim 1 in which DH<sub>a</sub> is



7. A composition according to any of Claims 1 to 6 which additionally contains an inert transparent polymeric binder for the dye and the triarylimidazolyl dimer.

10 8. A light-sensitive composition which comprises a composition according to any of Claims 1 to 7 and an inert solvent.

9. A light-sensitive composition according to Claim 8, substantially as herein described in any of the Examples.

10 10. A substrate coated with a composition claimed in any of Claims 1 to 9.

11. Paper impregnated or coated with a composition claimed in any of Claims 1 to 9.

12. A coated substrate according to Claim 10 substantially as herein described in any of the Examples.

13. A process of forming a colored material, which comprises irradiating a composition claimed in Claim 8 or 9 with light having a wavelength of from 2000 Å to 4200 Å.

14. A process of forming a colored material, which comprises irradiating a composition claimed in Claim 8 or 9 coated on a supporting substrate with light having a wavelength of from 2000 Å to 4000 Å, and then subjecting the irradiated composition to a fixing treatment.

15. A process of forming a colored material, which comprises irradiating paper impregnated or coated with a composition claimed in Claim 8 or 9 with light having a wavelength of from 2000 Å to 4000 Å, then subjecting the irradiation composition to a fixing treatment.

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16. A process according to any of Claims 13 to 15 substantially as herein described in any of the Examples.

17. Colored materials produced by a process claimed in any of Claims 13 to 16.

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